

## PATENT SPECIFICATION

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## (54) METHOD OF DECOMPOSING AMMONIA

(71) We, MITSUBISHI CHEMICAL INDUSTRIES LTD., a Japanese Company, of 5-2, Marunouchi 2-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of decomposing ammonia to form nitrogen and more particularly, it relates to a method of effectively removing ammonia in effluent gas by catalytic decomposition.

In many cases, ammonia is contained in effluent gas discharged from an industrial plant or a copying machine. The discharge of ammonia to the atmosphere causes pollution of the operational environment and also external air pollution.

It is quite important to remove ammonia from effluent gas. When the ammonia content in the discharged gas is relatively high, it is possible to apply an absorption method using dilute sulfuric acid.

However, when the ammonia content is relatively small and the total amount of the discharged gas is large, it has not been possible to find a suitable method of removing ammonia effectively. In the former absorption method, treatment of the discharged waste solution is required.

In an absorption method using a molecular sieve, it is required to apply complicated steps for reactivating the molecular sieve. The cost required for purification by these methods, is quite high.

It is known to use a method of catalytic decomposition of ammonia to form nitrogen as the principal end product.

In the known methods, the formation of toxic nitrogenous materials such as NO or NO<sub>2</sub> (hereinafter referred to as NO<sub>x</sub>) in the decomposition step is serious. In practice, these methods are insufficient as a detoxifying process.

The inventor of the present invention attempted to provide a method of efficiently decomposing ammonia in waste gas to form

nitrogen, and has found that ammonia can be easily decomposed to nitrogen without the formation of NO<sub>x</sub> by catalytic decomposition using a specific catalyst under specific conditions, whereby the waste gas can be detoxified.

It is an object of the present invention to provide a method of oxidative decomposition of ammonia to form nitrogen by a relatively simple operation.

It is another object of the invention to provide a method of treating an ammonia-containing gas discharged from a large size copying machine.

According to the invention there is provided a method of decomposing ammonia to form nitrogen which comprises catalytically contacting a gas mixture containing ammonia and oxygen, the molar ratio of oxygen to ammonia being 3:1 or more, with a ruthenium and/or a platinum catalyst at 150—400°C.

In the operation of the method of the invention, the gas mixture containing ammonia and oxygen can be diluted with an inert gas such as nitrogen. Inert gas means a gas which is not active in the oxidation reaction of ammonia.

It is preferable to use the method with a gas mixture containing a relatively small ammonia content such as 2% or less by volume of the total gas and an oxygen content of 1—22% by volume.

When the molar ratio of oxygen to ammonia in an effluent gas is within the range of the invention, the effluent gas can be directly treated by the method of the invention.

The gas discharged from diazo-type copying machines such as those used for copying various documents, e.g. office papers and slip plans, usually contains less than 2% of ammonia, usually 500—3,000 ppm of ammonia.

The catalytic method of the invention can be directly applied to such effluent gas.

The platinum or ruthenium of the metal component of the catalyst used in the invention is preferably supported on a carrier, such as one made of alumina, silica-alumina, silica, diatomaceous earth, titania or zirconia.

The production of NO<sub>x</sub> is dependent upon

the kind of carrier used for the platinum and/or ruthenium catalyst.

Under the same conditions, the production of  $\text{NO}_x$  increases in the order:  $\alpha$ -alumina, silica-alumina (low alumina content)  $\gamma$ -alumina, silica, silica-alumina (high alumina content).

Accordingly, it is preferable to use  $\alpha$ -alumina,  $\gamma$ -alumina or silica-alumina (low alumina content) as the carrier from the viewpoint of inhibiting the formation of  $\text{NO}_x$ .

The platinum and/or ruthenium supported on the carrier is usually in the range of 0.01—2% by weight of the carrier.

The shape of the carrier can be honeycomb, spherical or pellet-like in shape.

The catalyst supporting the platinum and/or ruthenium can be prepared by dipping the carrier in an aqueous solution containing a catalytic metal compound (e.g. chloride) and reducing the compound with a reducing agent such as formaldehyde or hydrazine in the liquid phase, or reducing the dried compound in a hydrogen atmosphere. The resulting catalyst is active at 150—400°C, preferably 150—300°C, especially 180—260°C.

Below 150°C, the catalytic activity is insufficient and above 400°C, the formation of  $\text{NO}_x$  is too high to attain the object of the invention.

The catalyst used in the invention can be used with a gas flow at a space velocity of 1000—100,000  $\text{hr}^{-1}$ , preferably 5,000—40,000  $\text{hr}^{-1}$ . Even though sufficient ammonia conversion can be attained by contacting the gas with a platinum or a ruthenium catalyst used singly, it is more effective to combine the steps of contacting the gas first with a ruthenium catalyst and then with a platinum catalyst, as the formation of both  $\text{NO}_x$  and  $\text{N}_2\text{O}$  can be decreased.

In a two step process of this invention, the ruthenium catalyst is used as the first catalyst

layer, wherein most of the ammonia is converted to nitrogen.

However, the gas passed from the first catalyst layer contains some by-product  $\text{NO}_x$ .

Accordingly, the gas is subsequently contacted with a platinum catalyst in the second catalyst layer to reduce the  $\text{NO}_x$  with the remaining ammonia to nitrogen.

The molar ratio of  $\text{NH}_3/\text{NO}_x$  in the gas fed to the second catalyst layer after the first catalytic reaction, is preferably in a range of 1—10:1. The temperature of each catalyst layer is selected from the range of 150—400°C. It is convenient to employ a single reactor filled with ruthenium and platinum catalysts in two layers.

The two step process of this invention has an advantage in reducing the formation of both  $\text{NO}_x$  and  $\text{N}_2\text{O}$  which would not be completely avoided by using either a ruthenium or a platinum catalyst singly.

As stated above, in accordance with the invention, ammonia in an effluent gas can be effectively decomposed to form nitrogen and water, whereby the gas containing ammonia can be detoxified and the operational environment can be improved and the air pollution can be prevented.

The invention will be further illustrated by reference to examples.

In the examples, the concentration of ammonia in the outlet gas discharged from the reactor was measured by collecting it in a dilute sulfuric acid trap and analyzing by a titration method using methyl orange as indicator. The concentration of  $\text{N}_2\text{O}$  was measured by gas chromatography and the concentration of  $\text{NO}_x$  was measured by the chemiluminescence method with a chemiluminescent  $\text{NO}_x$  analyzer (nitrogen oxide analyzer CLM-201 manufactured by Shimadzu Seisakusho K.K.). The  $\text{NH}_3$  conversion was calculated by the equation

$$\text{NH}_3 \% \text{ conversion} = \frac{\text{NH}_3 (\text{inlet}) - [\text{NH}_3 (\text{outlet}) + \text{NO}_x (\text{outlet})]}{\text{NH}_3 (\text{inlet})} \times 100$$

#### Example 1.

20 ml of pellet-type  $\alpha$ -alumina having a surface area of less than  $10 \text{ m}^2/\text{g}$ , a diameter of  $3/16''$  and a length of  $3/16''$  was immersed in 20 ml of an aqueous solution containing 0.893 g of chloroplatinic acid at room temperature for 16 hours. After drying the product at 90°C for 2 hours, samples of the product were reduced in a hydrogen atmosphere at 100°C, 200°C, 300°C and 400°C respectively for 1 hour each, to give an  $\alpha$ -alumina catalyst supporting 0.5 wt.% of platinum.

20 ml of the catalyst was charged to a reactor. Air containing 3,000 ppm of ammonia was introduced into the reactor at a rate of 200 l/hr, thus establishing a space velocity of

10,000  $\text{hr}^{-1}$ . The outlet gas discharged from the reactor was sampled and analyzed and the catalytic activity of the catalyst was measured. The results are shown in Table 1.

#### Example 2.

20 ml of pellet-type silica-alumina having a surface area of  $400 \text{ m}^2/\text{g}$ , a diameter of 6 mm and length of 5 mm (composition 86—88%  $\text{SiO}_2$ , 12—14%  $\text{Al}_2\text{O}_3$  and less than 0.1%  $\text{Fe}_2\text{O}_3$ ) was immersed in 20 ml of an aqueous solution containing 0.392 g of chloroplatinic acid at room temperature for 16 hours.

The product was treated in accordance with Example 1 to give a silica-alumina catalyst supporting 0.5 wt.% of platinum. The catalytic

activity of the resulting catalyst was measured by using 20 ml of the catalyst according to the procedures described in Example 1. The results are shown in Table 1.

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#### Example 3.

15 ml of spherical alumina having a surface area of 250–350 m<sup>2</sup>/g and a diameter of 4–6 mm (composition 0.2% Na<sub>2</sub>O, 0.03% SiO<sub>2</sub>, 97.5–98.7% Al<sub>2</sub>O<sub>3</sub>, 0.03% Fe<sub>2</sub>O<sub>3</sub> and 1.0–2.0% ignition loss) was immersed in 20 ml of an aqueous solution containing 0.172 g of chloroplatinic acid and treated in accordance with Example 1 to give a  $\gamma$ -alumina catalyst supporting 0.5 wt.% of platinum.

15 15 ml of the catalyst was charged to a reactor. Air containing 2,700 ppm of NH<sub>3</sub> was introduced to the gas inlet of the reactor at a rate of 150 l/hr, thus establishing a space velocity of 10,000 hr<sup>-1</sup>. The results of the analysis of the gas discharged are shown in Table 1.

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#### Example 4.

20 ml of pellet-type silica having a surface area of 150 m<sup>2</sup>/g, a diameter of 6 mm and a height of 5 mm (composition 93–95% SiO<sub>2</sub>, 0.5% Al<sub>2</sub>O<sub>3</sub>, 0.5% Fe<sub>2</sub>O<sub>3</sub> and 4–6% ignition loss) was immersed in 20 ml of an aqueous solution containing 0.31 g of chloroplatinic acid and treated in accordance with Example 1.

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The catalytic activity of the resulting catalyst is shown in Table 1.

#### Example 5.

35 The process of Example 1 was repeated using a pellet-type silica-alumina having a surface area of 250 m<sup>2</sup>/g, a diameter of 6 mm and a length of 5 mm (composition of 73–75% SiO<sub>2</sub>, 25–27% Al<sub>2</sub>O<sub>3</sub> and less than 1% Fe<sub>2</sub>O<sub>3</sub>) instead of  $\alpha$ -alumina.

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The catalytic activity of the resulting catalyst is shown in Table 1.

#### Example 6.

The process of Example 3 was repeated

using a pellet-type  $\gamma$ -alumina catalyst supporting 0.5 wt.% of ruthenium and having a diameter of 3 mm and a height of 3 mm.

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The catalytic activity of the resulting catalyst is shown in Table 1.

#### Example 7.

20 ml of the  $\gamma$ -alumina used in Example 3 was immersed in 20 ml of an aqueous solution containing 0.07 g of chloroplatinic acid and 0.062 g of ruthenium chloride at room temperature for 16 hours, and was treated in accordance with Example 3, to give a  $\gamma$ -alumina catalyst supporting 0.2% of platinum and 0.1% of ruthenium.

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The catalytic activity of the resulting catalyst was measured in accordance with Example 3.

The results are shown in Table 1.

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#### Example 8.

10 ml of a  $\gamma$ -alumina catalyst supporting 0.5% of ruthenium (diameter of 3 mm and height of 3 mm) prepared as in Example 6 was placed in a reactor as a first catalytic layer, and 5 ml of Pt-honeycomb-type  $\alpha$ -alumina catalyst coated with  $\gamma$ -alumina supporting 0.3% of platinum was added as a second catalytic layer.

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The Pt-honeycomb-type catalyst was prepared by dipping a honeycomb carrier made of  $\alpha$ -alumina in a  $\gamma$ -alumina slurry and sintering at 800–1,000°C to give  $\alpha$ -alumina carrier coated with  $\gamma$ -alumina and dipping the carrier in an aqueous solution of chloroplatinic acid and drying it and then reducing it to 300°C in a hydrogen atmosphere.

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Air containing 1,200 ppm of ammonia at 200°C and 220°C was introduced into the reactor at a rate of 200 l/hr.

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The outlet gas discharged from the reactor was sampled and analyzed and the catalytic activity of the catalyst was measured.

The results are shown in Table 1.

TABLE I

Example	Catalyst/carrier	NH <sub>3</sub> (inlet) (ppm)	Reaction temperature (°C)	Composition of outlet gas (ppm)				NH <sub>3</sub> conversion (%)
				NH <sub>3</sub>	NO <sub>x</sub>	N <sub>2</sub> O		
1	0.5% Pt/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	3000	210	163	5	400		94.4
			220	34	6	490		98.7
			230	6	6	590		99.5
2	0.5% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (low content of Al <sub>2</sub> O <sub>3</sub> )	3000	230	63	15	590		97.4
			240	34	20	730		98.2
3	0.5% Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2700	220	149	16	410		93.9
			230	49	33	570		97.0
4	0.5% Pt/SiO <sub>2</sub>	3000	230	214	24	560		92.1
			240	70	30	570		96.7
			250	20	41	660		98.0
5	0.5% Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> (high content of Al <sub>2</sub> O <sub>3</sub> )	2700	240	156	46	360		93.3
			250	70	70	440		95.3
6	0.5% Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2700	184	121	32	40		94.3
			205	17	85	40		96.2
			220	5	95	50		96.3
7	0.2% Pt 0.1% Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	2700	252	60	18	450		97.1
8	first layer 0.5% Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> second layer 0.3% Pt/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub> ( $\gamma$ -Al <sub>2</sub> O <sub>3</sub> coat)	1200	200	7	25	50		97.3
		1200	220	22	30	80		95.3

### Example 9-1.

400 ml of  $\gamma$ -alumina as used in Example 3 was immersed in 400 ml of an aqueous solution containing 4.587 g of chloroplatinic acid for 24 hours. The product was reduced with hydrazine and then washed with water and dried to give a  $\gamma$ -alumina catalyst supporting about 0.5 wt. % of platinum.

- 10 200 ml of  $\gamma$ -alumina was immersed in 200 ml of an aqueous solution containing 4.0 g of ruthenium chloride for 24 hours. The product was reduced with hydrazine and then washed with water and dried to give a  $\gamma$ -alumina catalyst supporting about 0.5 wt. % of ruthenium. 200 ml of the ruthenium catalyst was placed in a reactor made of stainless steel as a first catalyst layer and 400 ml of the platinum-type catalyst was added as a second catalyst layer. Air containing about 2500 ppm of ammonia was introduced in the

reactor at a rate of 8000 l/hr.

The outlet gas discharged from the reactor was sampled and analyzed and the catalytic activity of the catalyst was measured. The results are shown in Table 2.

### Example 9-2.

Air containing about 2500 ppm of ammonia was treated in accordance with the process of Example 9-1, using 200 ml of the ruthenium catalyst alone.

The results are shown in Table 2.

### Example 9-3.

Air containing about 2300 ppm of ammonia was treated in accordance with the process of Example 9-1, using only 400 ml of the platinum type catalyst.

The results are shown in Table 2.

TABLE 2

	Catalyst		Space velocity (hr <sup>-1</sup> )	Temperature in reactor		NH <sub>3</sub> (ppm)		NO <sub>x</sub> (ppm)	N <sub>2</sub> O (ppm)
	component	volume (ml)		inlet	outlet	inlet	outlet		
9-1	1st layer 0.5% Ru/ $\gamma$ -alumina	200	20,000	237	257	2500	5	28	250
	2nd layer 0.5% Pt/ $\gamma$ -alumina	200							
9-2	0.5% Ru/ $\gamma$ -alumina	200	40,000	220	248	2500	280	95	80
9-3	0.5% Pt/ $\gamma$ -alumina	400	20,000	233	255	2500	170	150	115
				228	253	2300	5.2	15.5	530

## WHAT WE CLAIM IS:—

1. A method of decomposing ammonia to form nitrogen which comprises catalytically contacting a gas mixture containing ammonia and oxygen, the molar ratio of oxygen to ammonia being 3:1 or more, with a ruthenium and/or a platinum catalyst at 150—400°C.
2. A method as claimed in claim 1, wherein the gas mixture is catalytically contacted first with a ruthenium catalyst and then with a platinum catalyst.
3. A method as claimed in claim 1 or claim 2, wherein the amount of ammonia in the gas mixture is 2% or less by volume of the total gas.
4. A method as claimed in any preceding claim, wherein the catalyst is used with a gas flow at a space velocity of 1,000—100,000 hr<sup>-1</sup>.
5. A method as claimed in claims 2 to 4, wherein the molar ratio NH<sub>3</sub>/NO<sub>x</sub> in the gas after passing through the first catalyst layer is in the range 1—10:1.
6. A method as claimed in any preceding claim, wherein the ruthenium and/or platinum is supported on a carrier in an amount within the range 0.01—2% by weight of the carrier.
7. A method as claimed in claim 1 substantially as described herein with reference to any one of the Examples.

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